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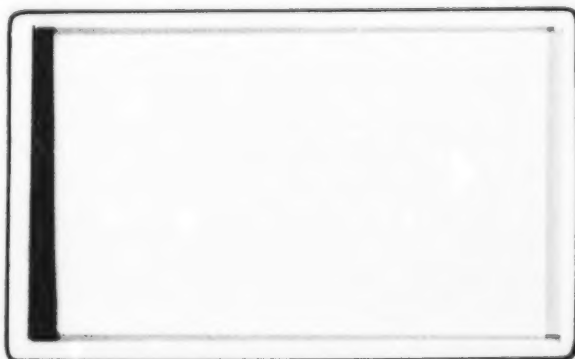
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By

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Environment Canada
Conservation and Protection
Environmental Protection
Saskatchewan District

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MERCURY SURVEY OF THE
SASKATCHEWAN RIVER SYSTEM
IN SASKATCHEWAN

Report CP(EP)WNR88/89-3

(i)

ABSTRACT

Total and methyl mercury concentrations are reported for sediments, biota and water collected during 1984 and 1985 from the Saskatchewan portion of the Saskatchewan River System. Historical information shows the South Saskatchewan River was contaminated with mercury, largely as a result of effluent from a chlor-alkali plant located in the City of Saskatoon, on the South Saskatchewan River. The present survey concentrates on the South Saskatchewan River below Saskatoon. Data show the former chlor-alkali plant, the City of Saskatoon sewage plant and nonpoint sources currently contribute low amounts of Hg to this river. Total Hg (dry wt.) concentrations in sediments along an 8.8 km reach of the South Saskatchewan River, downstream of the former chlor-alkali plant, have decreased from 1971 levels between 0.95 and 2.45 ug/g to current levels of less than 0.03 ug/g. Mercury concentrations in the surface sediments of this river are similar to Hg concentrations elsewhere in the Saskatchewan River System. Crayfish, macrophyte and water samples from the South Saskatchewan River contain low Hg concentrations. Sediments collected from Tobin Lake, the major sediment sink downstream, contain between 0.08 and 0.24 ug/g (dry wt.) of total Hg. Concentrations in Cumberland Lake, downstream of Tobin Lake, are between 0.01 and 0.08 ug/g (dry wt.).

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1.0 INTRODUCTION

The environmental and human health dangers of Hg in the form of methylmercury (CH_3Hg^+) surfaced in the 1960's from a major incident of chronic CH_3Hg^+ poisoning. This incident occurred when Japanese residents consumed fish, over a long period of time, that were contaminated by the industrial release of Hg into Minamata Bay. Other incidents of CH_3Hg^+ poisoning (Minamata Disease) have since been reported in other parts of the world.

Until the late 1960s, the release of inorganic Hg was not considered a threat to the environment. This concept changed with dual discoveries: that Hg in polluted fish occurs in the form of CH_3Hg^+ compounds (Westoo 1966 from Jonasson and Boyle 1979) and that inorganic Hg can be transformed to CH_3Hg^+ by microorganisms in the sediments (Jensen and Jernelöv 1969). The increasing awareness of the environmental significance of Hg, in any form, prompted several countries including Canada to control the industrial release of inorganic Hg into the environment. Consequently, between 1971 and 1981, the chlor-alkali industry, the major Hg user in Canada, reduced its annual liquid effluent losses of Hg from 3000 to 110 kg (Environment Canada 1983). Other sectors, like the pulp and paper industry and the agricultural community, have also discontinued their use of Hg.

Canadian ecosystems affected by the release of Hg from chlor-alkali production include the English-Wabigoon River System. This system received an estimated 9 to 11 tonnes of Hg, between 1962 and 1969, from a chlor-alkali plant at Dryden Ontario (Armstrong and Hamilton 1973). Surficial sediments have been an important Hg source to fish in this system and techniques have been investigated to reduce the Hg released from these sediments (Rudd *et al.* 1983). In comparison, the South Saskatchewan River received an estimated 22 to 33 tonnes of Hg, between 1963 and 1978, from a Saskatoon chlor-alkali plant (Beak Consultants Ltd. 1982). The concern for Hg in the environment in the late 1960's prompted several Hg studies of the South

Saskatchewan River. These studies (Wobeser et al. 1970; Sumner et al. 1972; Uthe et al. 1973) showed elevated levels of Hg in the skeletal muscle of some fish. High Hg concentrations were also reported in river sediments downstream of the chlor-alkali plant (Bailey et al. 1971; Hwang 1978). Although a major reduction in the discharge of Hg from this plant occurred in the early 1970's, Hg concentrations in South Saskatchewan River fish have remained high up to the time of this study. Mercury from contaminated sediments or some other source(s) may be responsible for this fish contamination.

2.0 PURPOSE

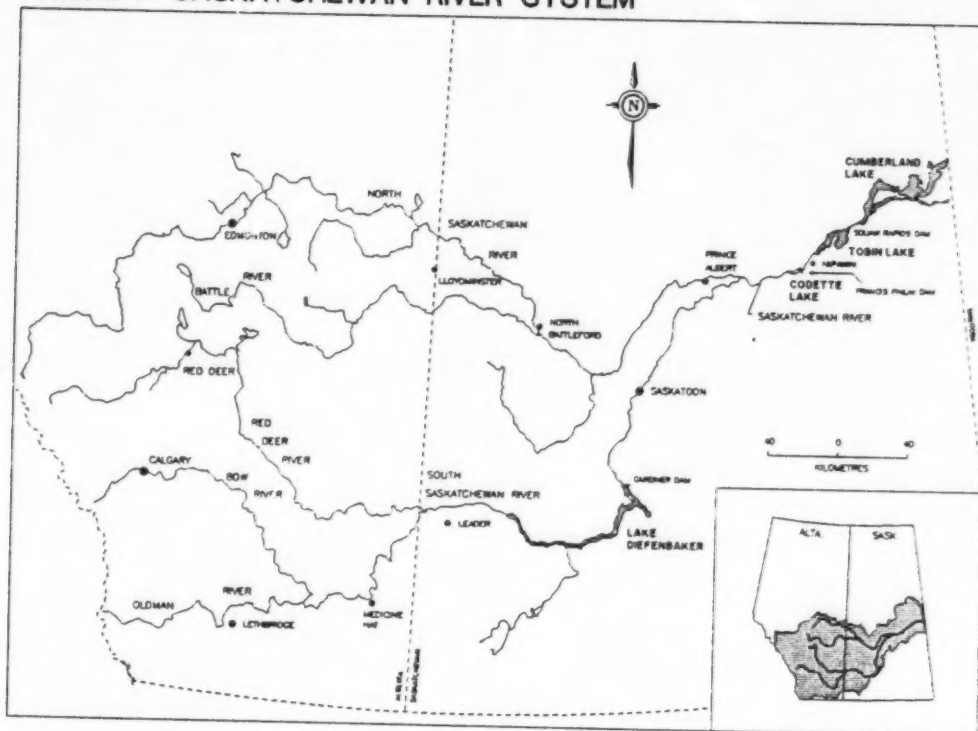
This report presents: 1) historical Hg data for the Saskatchewan River System and 2) 1984 and 1985 Hg data for sediment, biota and water collected from this river system with emphasis on the South Saskatchewan River below Saskatoon.

3.0 DESCRIPTION OF THE SASKATCHEWAN RIVER SYSTEM

The South Saskatchewan River is formed by the confluence of the Bow and Oldman Rivers in Alberta and is joined by the Red Deer River near the Alberta-Saskatchewan border (Figure 1). The Alberta Cities of Calgary, Lethbridge, Red Deer and Medicine Hat are the major municipal/industrial users in the sub-basin. The City of Saskatoon is the lone major Saskatchewan municipality on the South Saskatchewan River.

The Gardiner Dam is the only major Saskatchewan structure on the South Saskatchewan River. Lake Diefenbaker, formed by the completion of the Gardiner Dam in 1968, is a multipurpose reservoir. The regulation of Lake Diefenbaker, for hydroelectric power, has altered the downstream flow regime. The spring run-off is now stored, resulting in a significant reduction of the peak spring flow. The minimum desirable flow ($43 \text{ m}^3/\text{s}$) usually occurs in the summer and early fall (Richards 1980). The July and August mean flows recorded at Saskatoon, from 1975 to 1985, were 138 and

FIGURE 1 SASKATCHEWAN RIVER SYSTEM



133 m³/s respectively (Water Survey of Canada). Water released by the winter operation of the power plant vary from 250 to 350 m³/s (Prairie Provinces Water Board 1982). The maximum flow capacity from this plant is 425 m³/s.

Downstream from Lake Diefenbaker, the river bed material is a moderately well-sorted sand with a mean particle size diameter of 0.3 mm (Cant 1978). Minor amounts of fine gravel are present in a few deep channels, and silts and muds are common in sheltered areas on the lee sides of braided bars (Cant 1978). The river is composed of four major geomorphological units: 1) channels, 2) large bars, 3) sand flats, and 4) vegetated islands and floodplains (Cant 1978).

The Saskatchewan River is formed by the confluence of the North and South Saskatchewan Rivers, which respectively comprise 44 and 56 percent of its average annual flow at the confluence.

This river flows through a deep glacial spillway to Tobin Lake. Between Tobin Lake and the Saskatchewan-Manitoba border, the river flows through the Saskatchewan Delta. Cumberland Lake is a natural unregulated lake on the northern side of this delta.

There are two hydroelectric developments on the Saskatchewan River. The Squaw Rapids Dam controls the outflow from Tobin Lake, which was filled in the winter of 1961-62. The Francis Finlay Dam, completed in 1985, controls the outflow from Codette Lake.

4.0 LITERATURE

4.1 Introduction

Information regarding past and present Hg sources to the South Saskatchewan River was reviewed to: 1) estimate the amounts of Hg released; 2) determine the relative importance of each source; and 3) establish sampling locations downstream of the major source(s). Contributions from the chlor-alkali plant, the City of Saskatoon sewage plant and nonpoint sources were examined. Mercury data for fish, sediment and water from the Saskatchewan River System were also reviewed to assess the significance of the Hg results obtained in the 1984-1985 survey.

4.2 Mercury Sources To The South Saskatchewan River

4.2.1 Chlor-Alkali Plant

In 1962, a chlor-alkali plant commenced operation in Saskatoon under the ownership of Interprovincial Cooperatives. Ownership changed several times afterwards: 1) in 1970, to Northern Industrial Cooperatives; 2) in 1973, to Saskatoon Chemicals, a subsidiary of Prince Albert Pulp Co. Ltd.; and 3) in 1986, to Weyerhaeuser Canada Limited. This plant is referred to herein as Saskatoon Chemicals. The plant is located on the north bank of the South Saskatchewan River, approximately 8.2 km

downstream from the river weir at Saskatoon, or 1.3 km downstream from the outfall of the Saskatoon sewage treatment plant.

Between 1963 and 1978, the plant discharged an estimated 22 to 33 tonnes of Hg into the South Saskatchewan River (Beak Consultants Ltd. 1982). As shown in Table 1, the highest release of Hg occurred in the late 1960's. This was due to a plant expansion in 1968. By 1970, the Hg release was sharply curtailed to meet effluent quality limits. Thereafter, the Hg reduction was more gradual as shown in Figure 2. In November 1978, the mercury cells were replaced with membrane cells which eliminated the use of Hg in the process. This conversion resulted in a further estimated decrease of Hg in the effluent: from 0.018 kg/day, in 1978, to 0.004 kg/day, in 1981 (Beak Consultants Ltd. 1982). This 1981 rate (0.004 kg/day) corresponds to a 0.003 ug/L increase in the background Hg concentration of the South Saskatchewan River when the mean river flow is 180 m³/s (Water Survey of Canada 1981-1984 data).

TABLE 1
CHLOR-ALKALI PLANT EFFLUENT DISCHARGE OF MERCURY

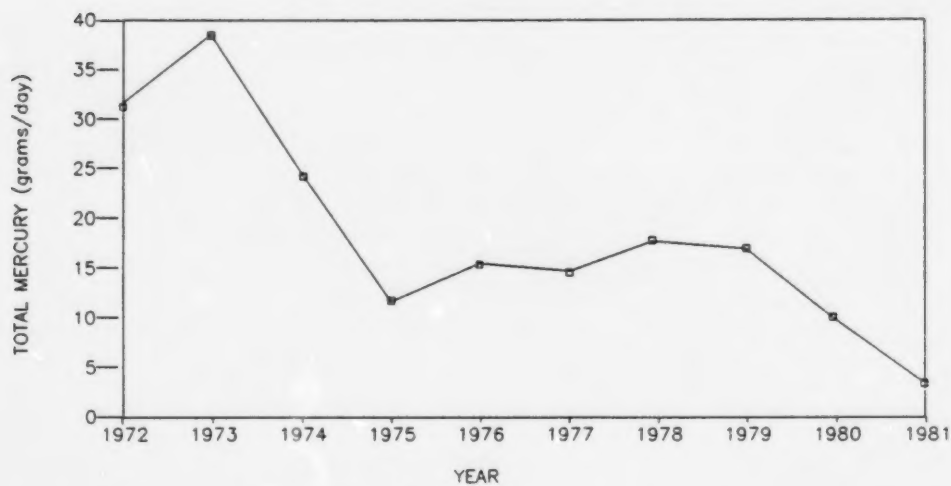
Period	Hg (kg/day)
1963 - 1967	7-9
1968 - 1969	14-23
1970	0.7
1974 - 1978	0.010-0.018
1981	0.004

1963 - 1978	estimated total: 22-33 tonnes

Reference: Beak Consultants Ltd. (1982)

Plant air emissions contained an estimated 1.27 kg/day of Hg in 1976 (Beak Consultants Ltd. 1976 from Beak Consultants Ltd. 1982) and decreased to <0.00003 kg/day in 1981 (Beak Consultants Ltd. 1982). This 1981 rate is considered negligible compared to the 0.004 kg/day of Hg released directly into the South Saskatchewan River.

FIGURE 2 MERCURY EFFLUENT LOADING FROM SASKATOON CHEMICALS



Reference: Beak Consultants Ltd. (1982)

4.2.2 Municipal Sewage

Municipal sewage is another pathway for Hg entry to the South Saskatchewan River. The average total Hg concentration for the City of Saskatoon sewage plant effluent (C.P. Hwang, Plant Engineer, pers. comm. April 1985) is significantly diluted by the river. For instance, for a river flow of $180 \text{ m}^3/\text{s}$, the river background concentration of Hg is increased by only 0.001 ug/L .

4.2.3 Nonpoint Sources

Between 1930 and 1972, an estimated 54 to 108 tonnes of elemental Hg were placed on Saskatchewan soils from seed treatment practices (Fehr and Dennis 1973). Pollution of the South Saskatchewan River by this Hg, however, is considered negligible due to the small Hg increase in the background soil concentration that occurred (Fehr and Dennis 1973). Furthermore, this and other nonpoint Saskatchewan sources are considered insignificant since ninety-two percent of the average annual flow of the South Saskatchewan River at Saskatoon originates from sources in Alberta (Prairie Provinces Water Board 1982).

4.2.4 Summary

The former chlor-alkali plant contributed the majority of Saskatchewan's anthropogenic Hg to the South Saskatchewan River. Much of this Hg has been dispersed by river sediments and waters. Currently, the chlor-alkali plant, the Saskatoon sewage plant and nonpoint sources are not considered significant Hg sources to the South Saskatchewan River. To determine the importance of bottom sediments as a nonpoint Hg source, the survey focused on the South Saskatchewan River below Saskatoon.

4.3 Historical Mercury Data

This section reports Hg data on fish, sediment and water for the Saskatchewan River System.

4.3.1 Mercury in Fish

Fish accumulate Hg in waters with low concentrations and thus are an excellent indicator for assessing the degree of aquatic Hg contamination. Mercury concentrations of 0.60 ug/g (wet wt.) in Northern Pike have been observed in waters which contain less than 0.005 ug/L of Hg (Bodaly et al. 1984).

Several fish surveys have been conducted on the Saskatchewan River System. Historical mercury data for fish species common to these surveys are summarized in Tables 2 to 4 for: 1) the North Saskatchewan River in Alberta; 2) two segments of the South Saskatchewan River; and 3) Tobin Lake. Definite conclusions cannot be drawn from these data due to differences in sampling and analytical techniques and the scant data available. However, some general observations can be made. The highest Hg concentrations are observed in South Saskatchewan River fish downstream of Saskatoon (Table 4). These high levels have been previously attributed to the chlor-alkali plant (Uthe et al. 1973). Upstream at Leader, near the Alberta-Saskatchewan border, Hg levels in fish are generally lower (Table 4). Downstream,

TABLE 2
TOTAL MERCURY (ug/g wet wt.) IN FISH -
NORTH SASKATCHEWAN RIVER

Year	Northern Pike	Walley	Goldeye	Reference
1973 ^a	0.45 (N ^d =10)	0.48 (N=3)	1.02 (N=141)	Munson (1978)
1974 ^a	0.32 (N=5)	0.34 (N=20)	0.86 (N=18)	
1975 ^a	0.40 (N=7)	0.69 (N=8)	0.59 (N=76)	
1976 ^a	0.34 (N=5)	0.59 (N=5)	0.65 (N=48)	
1982 ^b	---	0.37 (N=8)	0.45 (N=10)	Ramamoorthy <u>et al.</u> (1985)
1982 ^c	0.31 (N=43)	0.65 (N=35)	0.59 (N=69)	
a	Fish caught near Edmonton		c	Fish caught downstream of Edmonton
b	Fish caught upstream of Edmonton		d	No. of samples

TABLE 3
TOTAL MERCURY (ug/g wet wt.) IN FISH - TOBIN LAKE

Year	Northern Pike	Walleye	Goldeye	Reference
1970	0.86 (N=10)	---	0.42 (N=16)	Sumner <u>et al.</u> (1972)
1974 ^a	---	1.14 (N=23)	0.84 (N=51)	Munson (1978)
1975 ^a	---	0.92 (N=7)	0.62 (N=32)	
1978	0.78 (N=10)	1.08 (N=16)	0.33 (N=9)	Saskatchewan Environment and Public Safety (unpublished data)
1979	1.27 (N=9)	1.86 (N=11)	0.71 (N=9)	
1980	0.66 (N=6)	1.56 (N=15)	0.40 (N=12)	
1981	0.69 (N=7)	0.76 (N=12)	0.42 (N=2)	
1982	---	0.72 (N=10)	---	
^a Fish caught at Nipawin				

Tobin Lake Pike and Walleye (Table 3) are higher than corresponding fish from the North Saskatchewan River (Table 2) and Leader (Table 4). These three areas show similar Hg concentrations for Goldeye.

4.3.2 Mercury in Bottom Sediments

Due to their low water solubility, inorganic and organic Hg compounds released into the aquatic environment are sorbed on

TABLE 4
TOTAL MERCURY (ug/g wet wt.) IN FISH -
SOUTH SASKATCHEWAN RIVER IN SASKATCHEWAN

Location (Year)	Northern Pike	Walleye	Goldeye	Reference
Leader ^a				
(1970)	0.80 (N ^b =10)	1.46 (N=2)	0.45 (N=10)	Saskatchewan Parks, Recreation and Culture (unpublished data)
(1971)	0.80 (N=1)	1.30 (N=2)	0.51 (N=10)	
(1973)	0.70 (N=1)	---	0.67 (N=5)	
(1974)	0.60 (N=1)	0.86 (N=2)	0.23 (N=23)	
(1980)	0.24 (N=3)	1.57 (N=1)	---	
(1981)	---	0.76 (N=3)	0.39 (N=7)	
(1982)	0.29 (N=1)	0.48 (N=4)	---	
(1985)	0.31 (N=1)	0.48 (N=2)	0.27 (N=10)	
Clarkboro ^c				
Ferry (1969)	9.1 (N=3)	4.9 (N=2)	4.2 (N=2)	Wobeser <u>et al.</u> (1970)
Clarkboro				
Ferry 1970)	4.8 (N=3)	---	2.05 (N=5)	Sumner <u>et al.</u> (1972)
Clarkboro				
Ferry				Saskatchewan Parks, Recreation and Culture (unpublished data)
(1970)	4.15 (N=17)	---	1.63 (N=10)	
(1971)	3.27 (N=22)	---	2.88 (N=9)	
(1972)	---	---	2.40 (N=1)	
(1973)	1.42 (N=14)	1.20 (N=1)	1.16 (N=4)	
(1974)	1.72 (N=21)	---	---	
(1975)	2.44 (N=8)	---	---	
(1976)	1.11 (N=13)	1.15 (N=1)	1.63 (N=1)	
(1977)	0.87 (N=2)	---	1.25 (N=6)	
(1978)	1.77 (N=10)	---	---	
(1979)	2.54 (N=3)	1.99 (N=3)	1.49 (N=10)	
(1980)	0.93 (N=8)	1.06 (N=3)	1.51 (N=8)	
(1981)	1.15 (N=10)	2.09 (N=4)	1.27 (N=10)	
(1982)	1.12 (N=10)	0.63 (N=2)	1.53 (N=7)	
(1986)	0.65 (N=10)	0.84 (N=6)	0.88 (N=7)	

- a Upstream of Lake Diefenbaker
b No. of samples
c Downstream of Saskatoon

suspended particulates which settle in streams and lakes (Wallace et al. 1971). In freshwater systems, natural Hg levels may vary according to surrounding geology. Natural Hg levels in lake sediments are estimated at less than 0.06 ug/g (Harriss 1971). The natural Hg level in English-Wabigoon River sediments is 0.1 ug/g (Armstrong and Hamilton 1973).

Historical Hg sediment data for the Saskatchewan River System are summarized in Table 5. All sediment data are reported on a dry wt. basis. Mean total Hg concentrations for the Alberta

TABLE 5
TOTAL Hg (ug/g dry wt.) IN SASKATCHEWAN RIVER SYSTEM SEDIMENTS

Location	Range	Reference
<u>North Saskatchewan River</u>		
1) Upstream of Edmonton to Alta.-Sask. border	0.05-0.14 (N ^a =7)	Munson and Daniel (1973)
2) Downstream of Edmonton to Alta.-Sask. border	0.06-0.12 (N=9)	
Location	Mean	Reference
1) Upstream of Edmonton to central Edmonton	0.053 (N=35)	Ramamoorthy <u>et al.</u> (1985)
2) Central Edmonton to Fort Saskatchewan	0.074 (N=6)	
3) Fort Saskatchewan to Redwater R.	0.105 (N=4)	
4) Redwater R. to Alta.-Sask. border	0.092 (N=63)	
<u>South Saskatchewan R.</u>		
1) Upstream of Saskatoon Chemicals (SC)	0.033 (N=12)	Bailey <u>et al.</u> (1971)
2) 0-3.2 km downstream of SC	1.60 (N=43)	
3) 3.2-4.9 km downstream of SC	0.95 (N=23)	
4) 4.9-6.6 km downstream of SC	1.00 (N=12)	
5) 6.6-8.8 km	2.45 (N=20)	
6) Clarkboro Ferry (west side)	0.68 (N=4)	
(east side)	0.11 (N=4)	
1) Upstream of Saskatoon sewage plant	0.0078	Hwang (1978)
2) Upstream of SC	0.0228	
3) 0.5 km downstream of SC	0.2751	
4) Clarkboro Ferry (west side)	0.1388	
(east side)	0.0244	

^a No. of samples

portion of the North Saskatchewan River, sampled in 1981, ranged between 0.053 and 0.105 ug/g (Ramamoorthy et al. 1985). These values are similar to earlier concentrations reported by Munson and Daniel (1973) for the same reach of the river. The background concentration in the North Saskatchewan River, upstream of "central Edmonton", was 0.053 ug/g (Ramamoorthy et al. 1985).

In 1971, Bailey et al. (1971) reported high Hg concentrations along an 8.8 km reach of the South Saskatchewan River immediately downstream of Saskatoon Chemicals (Table 5). In 1978, Hwang (1978) found lower Hg sediment concentrations over this same reach (Table 5). Thus, over seven years there was a marked Hg reduction in the sediments immediately downstream of Saskatoon Chemicals. This reduction may be attributed to factors that include sediment erosion, the release of Hg to the water and atmosphere, and differences in sampling and analytical techniques.

Historical background Hg concentrations for the South Saskatchewan River upstream of Saskatoon Chemicals are similar to those for the North Saskatchewan River upstream of "central Edmonton": 0.033 ug/g (Bailey et al. 1971) and 0.0228 ug/g (Hwang 1978) vs 0.053 ug/g (Ramamoorthy et al. 1985).

4.3.3 Mercury in Water

Historical Hg data are available for the North and South Saskatchewan Rivers from two water quality networks and from a 1982 survey of the North Saskatchewan River.

One water quality network, managed by Environment Canada, includes total Hg data for two monitoring stations on the North and South Saskatchewan Rivers near the Alberta-Saskatchewan border. Data from these two stations, for the period 1974 to 1984, are mostly below 0.02 ug/L (Prairie Provinces Water Board 1987). The second water quality network, operated by Saskatchewan Environment and Public Safety, includes four water quality

stations on the South Saskatchewan River. Mercury values at these four stations are markedly higher than upstream values at the Environment Canada station for the period 1981-1984 (Table 6). This apparent discrepancy may be attributed to the "questionable results" which were assigned by Saskatchewan Environment and Public Safety to its data.

Ramamoorthy et al. (1985) collected total Hg water data for the North Saskatchewan River in Alberta between December 1981 and August 1982. Arithmetic mean concentrations from 0.09 ug/L (N=9) to 0.30 ug/L (N=16) of total Hg were reported for 117 unfiltered water samples from nine stations along a 600 km reach of this river (Table 6). During this same period, all eight total Hg concentrations at the Environment Canada station were less than 0.02 ug/L (Prairie Provinces Water Board 1987). Ramamoorthy et al. (1985) did not use the Environment Canada data to interpret their total Hg results, which were used to calculate Hg partition coefficients between fish, water and sediments.

5.0 DESCRIPTION OF STUDY AREA

The locations of the 54 sediment sampling stations are shown in Figure 3. Background sampling locations on the upper reach of the South Saskatchewan River were represented by Region 1 (Stations 1 to 4). Region 2 (Stations 5 to 14), downstream of a former chlor-alkali plant, included the Hg contaminated reach of the South Saskatchewan River previously reported. Region 3 (Stations 15 to 24) was located at sediment deposition sites on the South Saskatchewan River that included ferry crossings and river inlets. Region 4 (Stations 25 to 31) was established to provide background Hg data for Codette Lake. Region 5 (Stations 32 to 41) was comprised of substations located along transects on Tobin Lake. Region 6 (Stations 42 to 51) was located beyond the mouth of the Cumberland Delta including some stations off the lake. Region 7 (Stations 52 to 54), on the North Saskatchewan River, was located downstream of the City of Prince Albert and

TABLE 6
TOTAL Hg (ug/L) IN WATER (1981-1984)

Location	No. of Samples	No. of Values Below Detection Limit ^a	(75th Percentile)	Maximum Value
<u>S. Sask. R.</u>				
Leader ^b	17	4	0.07	1.02
Upstream of Saskatoon Sewage Plant ^b	17	8	0.04	0.2
Clarkboro Ferry ^b	29	10	0.10	6.0
Birch Hills Ferry ^b	12	5	0.06	0.26
HWY 41 ^c	43	39	<0.02	0.19

N. Sask. R.

Deer Creek ^c	20	19	<0.02	0.02
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Location	No. of Samples	No. of Values Below Detection Limit ^a	Mean	Maximum Value
Upstream of Edmonton at Blackmud Creek ^d	9	0	0.09	0.17
Upstream of Edmonton at Devon ^d	7	0	0.22	0.59
Edmonton at: Quensel Bridge ^d	16	0	0.30	1.58
Cloverbar Bridge ^d	16	0	0.19	0.65
Cloverbar Sewage ^d	13	0	0.22	0.80
Fort Sask. ^d	12	0	0.11	0.30
Redwater River ^d	14	0	0.22	1.22
Myrnam Bridge ^d	16	0	0.21	0.65
Lea Park ^d	14	0	0.19	0.63

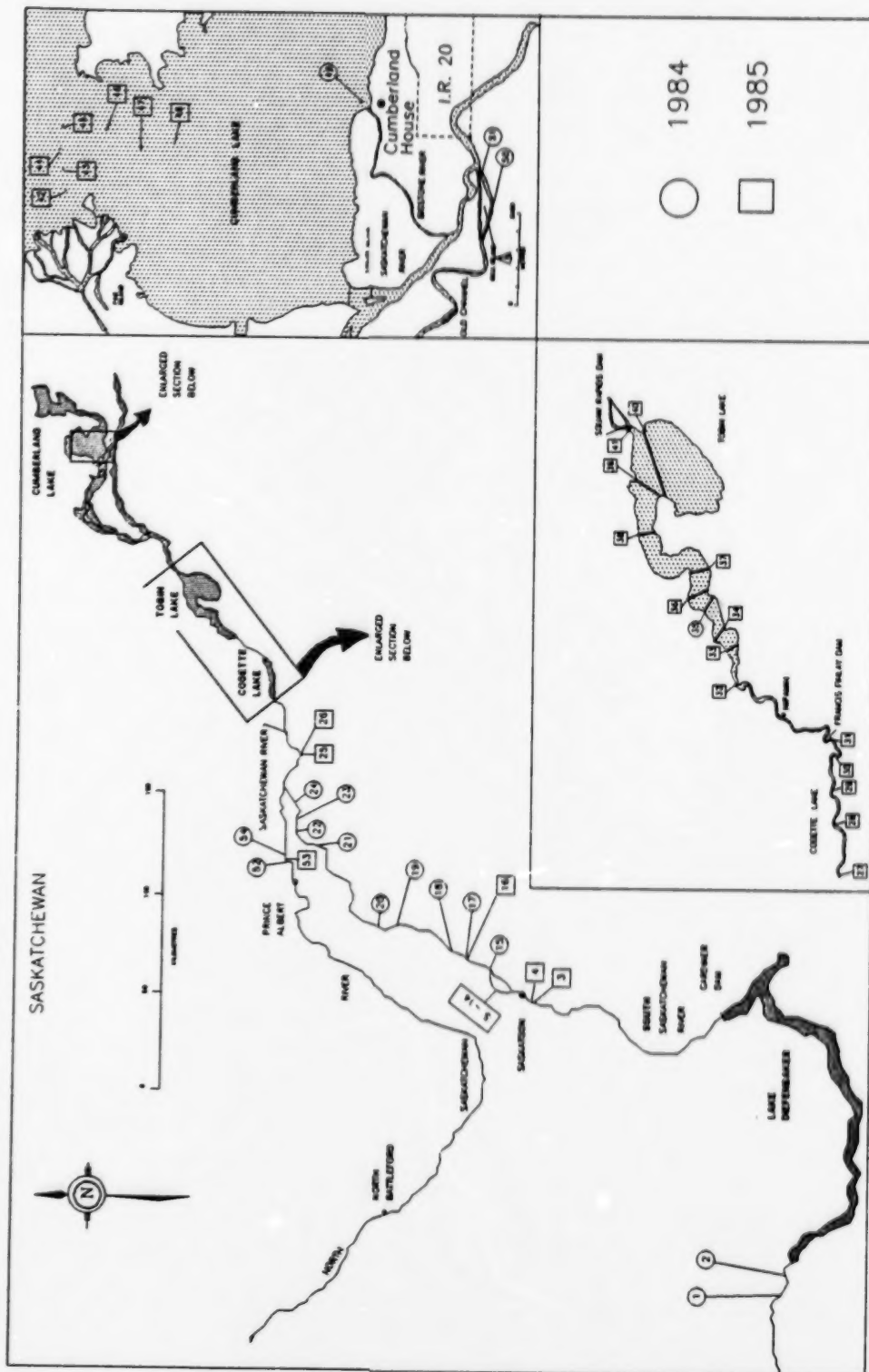
a <0.02 ug/L

b Saskatchewan Environment Esquadat data

c Environment Canada Naquadat data

d Ramamoorthy et al. (1985)

FIGURE 3 SAMPLING LOCATIONS



near the Weyerhaeuser pulp and paper mill; both are major effluent sources to this river.

6.0 METHODS

Sediment samples were collected at 54 stations. Water, crayfish and macrophyte samples were also collected at some stations. Seventeen stations were sampled in July 1984 and the other stations were sampled in August and September 1985.

6.1 Field Methods

6.1.1 Sediments

A Livingston piston corer was used to collect samples from most of the river stations. A KB corer and Ekman grab were used to collect sediments from Tobin Lake and Lake Diefenbaker. A Ponar grab was used to collect sediments from Codette Lake. A composite sample was taken at most of the 54 stations. Details on sampling methods and station locations are presented in Appendix 1. Each station sample was split in two fractions, placed in Whirlpac® plastic bags and frozen with dry ice for subsequent analyses. Typical core sample depths were between 10 and 12 cm for the river sediments and between 15 and 30 cm for the lake sediments.

6.1.2 Water

Water samples were taken at all 17 stations sampled in July 1984. At Stations 2 and 35, single grab samples were taken at mid depth (3 meters) with a Van Dorn sampler. Shallow waters were grab-sampled using sample bottles. All samples for total Hg were kept in acid-rinsed polyethylene bottles and preserved with HNO_3 (to pH 0.5) and 5% $\text{K}_2\text{Cr}_2\text{O}_7$. Grab samples for the nonmercury parameters were collected in polyethylene bottles. All samples were shipped, on ice, to the laboratory.

In 1985, grab samples for total Hg and CH_3Hg^+ were collected at Stations 3, 5 to 10 and 14. Samples for total Hg were collected in polyethylene bottles and preserved with 2 ml of concentrated H_2SO_4 and 2 ml of 5% $\text{K}_2\text{Cr}_2\text{O}_7$. Samples for CH_3Hg^+ were collected in glass bottles and preserved with 2 ml of concentrated H_2SO_4 . All samples were shipped, on ice, to the laboratory.

6.1.3 Biota

Four species of macrophytes (Polygonum coccineum, Scirpus sp., Potamogeton Richardsonii and Potamogeton pectinatus) were collected from the shorelines of most of the stations sampled in 1984. A minimum of six plants was collected and immediately frozen with dry ice. Plant leaves were later removed, freeze-dried and homogenized with a blender.

Crayfish specimens were caught near the stations with a minnow net and preserved in formaldehyde for up to three days. The abdominal muscles of the specimens were then removed and frozen in Whirlpac® plastic bags.

6.2 Laboratory Methods

6.2.1 Sediments

The 1984 sediment samples were split in two fractions in the field. One fraction was analyzed by the National Water Research Institute (NWRI) Laboratory, in Winnipeg, for total Hg using flameless atomic absorption spectrophotometry (Armstrong and Uthe 1971) and for CH_3Hg^+ using gas chromatography (Uthe et al. 1972). Analytical detection limits for total Hg and CH_3Hg^+ were 0.01 ug/g (dry wt.) and 0.10 ng/g (dry wt.) respectively. The other fraction was analyzed by the Environmental Protection (EP) Laboratory, in Edmonton, for: 1) iron (Environmental Protection Agency (EPA) 1979, method 236.1); 2) manganese (EPA 1979, method

243.1); 3) total carbon (American Public Health Association (APHA) 1980, method 209 G); 4) total kjeldahl nitrogen (Jackson 1958); 5) chloride (Edwards et al. 1981); and 6) particle size (Black et al. 1965).

The 1985 sediment samples were also split in two fractions in the field. The NWRI Laboratory analyzed one fraction for total Hg and CH_3Hg^+ using the above-noted analytical procedures. The EP Laboratory analyzed the other fraction for particle size (Black et al. 1965).

6.2.2 Water

The 1984 water samples were analyzed by the EP Laboratory for: 1) total Hg (EPA 1979, method 245.1); 2) iron and manganese (see 6.2.1); 3) total organic carbon (APHA 1980, method 505); 4) total kjeldahl nitrogen (EPA 1979, method 351.3); 5) $\text{NO}_2\text{-N}$ (EPA 1979, method 353.2); 6) $\text{NO}_3\text{-N}$ (EPA 1979, method 353.2); 7) chloride (EPA 1979, method 325.2); 8) total nonfilterable residue (APHA 1980, method 209 D); and 9) volatile nonfilterable residue (APHA 1980, method 209 G). The detection limit for total Hg was 0.20 ug/L.

The 1985 water samples were analyzed for total Hg and CH_3Hg^+ . The National Water Quality Laboratory of Environment Canada, in Burlington Ontario, analyzed water samples for total Hg (Environment Canada 1979). The detection limit for total Hg was 0.02 ug/L. The NWRI Laboratory analyzed for CH_3Hg^+ according to the following procedure: CH_3Hg^+ was rendered soluble by H_2SO_4 , which was then continuously extracted by an upward flow of condensed benzene in a liquid-liquid extractor for at least 6 hours. The benzene layer was separated and extracted with aqueous thiosulfate. Potassium iodide was then added and the resulting methylmercury iodide was re-extracted into benzene and analyzed by gas chromatography using an electron capture detector. The CH_3Hg^+ detection limit was 0.05 ng/L.

6.2.3 Biota

Macrophyte and crayfish samples were analyzed by the NWRI Laboratory for total Hg and CH_3Hg^+ . These samples were analyzed by the above-noted analytical procedures used for the sediments.

6.3 Laboratory Quality Control For Mercury

The quality control program consisted of the analyses of: 1) laboratory and field duplicates for analytical precision and 2) the analyses of standards for analytical accuracy. Precision was expressed as the average of the coefficients of variation, and accuracy was expressed as the average of the relative errors. The coefficient of variation is the standard deviation as a percentage of the mean, and the relative error is the difference between the measured and actual amounts as a percentage of the actual amount. The results of this program are presented in Table 7.

7.0 RESULTS

7.1 Bottom Sediments

Total and methyl mercury sediment concentrations are reported on a dry weight basis.

7.1.1 Total Mercury

Total Hg levels in Region 1 (Stations 1 to 4) range between 0.01 and 0.06 ug/g (Figure 4). Stations 1 and 2 are located at the upper end of Lake Diefenbaker in sediments that exceed 80% clay and silt. In contrast, Stations 3 and 4, just upstream of Saskatoon, have a clay and silt content less than 13%. These low clay and silt contents are consistent with the sandy bedform previously reported downstream of Lake Diefenbaker (Cant 1978). The high clay and silt contents at Stations 1 and 2 indicate Lake Diefenbaker serves as an effective trap for sediment-bound Hg.

TABLE 7
LABORATORY QUALITY CONTROL RESULTS FOR MERCURY

	Accuracy ^a	Precision ^b
<u>Sediments</u>		
Total Hg	10.2% (11) ^c	4.7% (23) ^d
CH ₃ Hg ⁺	ND ^f	15.3% (11) ^e
		35.3% (11) ^e
<u>Water</u>		
Total Hg	ND	LD ^g (2) ^e
CH ₃ Hg ⁺	ND	13.8% (2) ^e
<u>Crayfish</u>		
Total Hg	11.6% (4) ^c	ND
CH ₃ Hg ⁺	ND	ND
<u>Macrophytes</u>		
Total Hg	9.3% (2) ^c	13.2% (3) ^d
		13.7% (5) ^e
CH ₃ Hg ⁺	ND	25.7% (5) ^e

- a Average relative error of standards
- b Average coefficient of variation of duplicates
- c Number of standards
- d Number of laboratory duplicates
- e Number of field duplicates
- f Not Determined
- g Both less than detectable

Region 2 (Stations 5 to 14), below Saskatoon Chemicals, includes the 8.8 km reach of the South Saskatchewan River which previously possessed high Hg levels. Total Hg levels in Region 2 and Region 1 are similar: <0.01-0.03 ug/g vs 0.01-0.06 ug/g respectively. The sand content of Region 2 sediment is over 93% and is similar to the sand content of Stations 3 and 4 in Region 1.

Total Hg concentrations are generally higher in Region 3 (Stations 15 to 24) than in Region 2: 0.01 to 0.14 vs <0.01 to 0.03 ug/g. Except for the sandbar sampled at Station 16, Region 3 stations were located at river inlets or the downstream side of ferry crossing berms. These quiescent zones promoted the deposition of a greater amount of the finer sized sediments than found in Region 2 samples; the clay and silt content averaged 35% in Region 3 compared to an average 3% in Region 2. As shown in

FIGURE 4 TOTAL Hg (ug/g dry wt.) IN SASKATCHEWAN RIVER SYSTEM SEDIMENTS

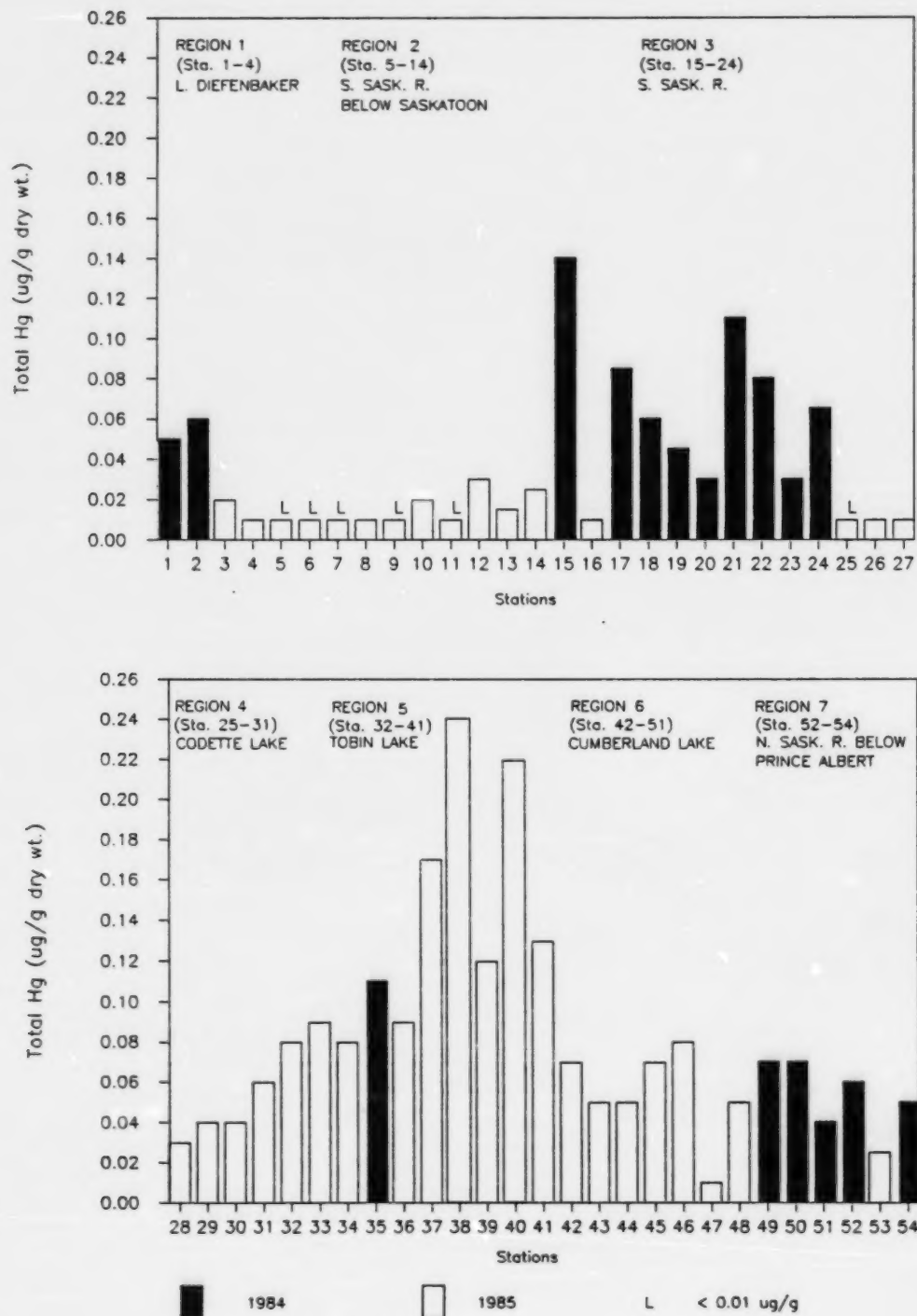


Figure 4, the lowest Hg value is at Station 16. This Hg value (0.01 ug/g) coincides with the lowest clay and silt content (4%) in Region 3.

Total Hg levels in sediments from Region 4 (Stations 25 to 31) are between <0.01 and 0.06 ug/g. These samples generally show higher Hg concentrations (ug/g) with increasing clay and silt content (%): <0.01 ug/g (5%), 0.01 ug/g (3%), 0.01 ug/g (2%), 0.03 ug/g (42%), 0.04 ug/g (61%), 0.04 ug/g (50%), and 0.06 ug/g (88%). Five of the samples (Stations 27 to 31) are from Codette Lake, which was filling at the time of sampling in September 1985. Reservoir creation for hydroelectric developments is of potential environmental concern since naturally occurring Hg in soils, innudated by water, are released and accumulated in reservoir fish (Bodaly et al. 1984). Therefore, these samples may serve as background data for future Hg investigations of this region.

The highest total Hg levels in the Saskatchewan River System are in Tobin Lake, represented by Region 5 (Stations 32 to 41). Historically, Tobin Lake has been the major sink for sediments transported down the North Saskatchewan River and the South Saskatchewan River below Lake Diefenbaker. Mercury in surficial Tobin Lake sediments range between 0.08 and 0.24 ug/g (Figure 4). Although these values are not appreciably greater than the highest values in Regions 2 and 3, the lower values in Tobin Lake generally exceed most of the values in Regions 1 and 2. The clay and silt content in Region 5 sediments is between 85 and 99%.

Some Region 5 sediments were analyzed at various depths as shown in Table 8. All four subsample cores comprising the top fraction (0-13 cm) for Station 34 contain 0.08 ug/g of total Hg. Similar subsamples for Station 36 show moderate total Hg variation: 0.11 ug/g, 0.12 ug/g, 0.06 ug/g and 0.09 ug/g. The concentration profiles of Stations 35, 37, 39 and 41, as well as eight subsamples of Stations 34 and 36, show that the Hg concentrations in the top fractions are generally less than or

similar to the lower fractions.

Region 6 comprised seven stations (Stations 42-48) on Cumberland Lake and another three (Stations 49-51) just off the lake. Total Hg levels in Region 6 are generally lower than

TABLE 8
MERCURY PROFILE OF TOBIN LAKE SEDIMENTS

Station	Depth (cm)	Total Hg ug/g (dry wt.)	CH ₃ Hg ⁺ ng/g (dry wt.)
34a	0-13	0.08	0.44
	13-28	0.10	0.10
34b	0-13	0.08	0.40
	13-23	0.10	<0.10
	23-35	0.11	<0.10
34c	0-13	0.08	0.50
	13-25	0.08	0.56
34d	0-13	0.08	<0.10
	13-23	0.09	<0.10
	0-15	0.11	0.64
	15-40	0.17	0.48
36a	0-13	0.11	0.52
	13-23	0.21	0.84
36b	0-13	0.12	<0.10
	13-23	0.11	0.38
	23-33	0.11	<0.10
36c	0-13	0.06	0.57
	13-25	0.16	0.41
	25-32	0.24	0.34
36d	0-13	0.09	0.48
	13-23	0.11	<0.10
	23-36	0.22	0.67
37	0-13	0.17	0.52
	13-20	0.25	0.53
39	0-12	0.12	0.75
	12-18	0.23	0.63
41	0-13	0.13	0.57
	13-25	0.14	0.48
	25-33	0.14	0.75

values in Region 5: 0.01-0.08 ug/g vs 0.08-0.24 ug/g. The clay and silt content of Region 6 is between 42 and 93% and is generally lower than that of Region 5.

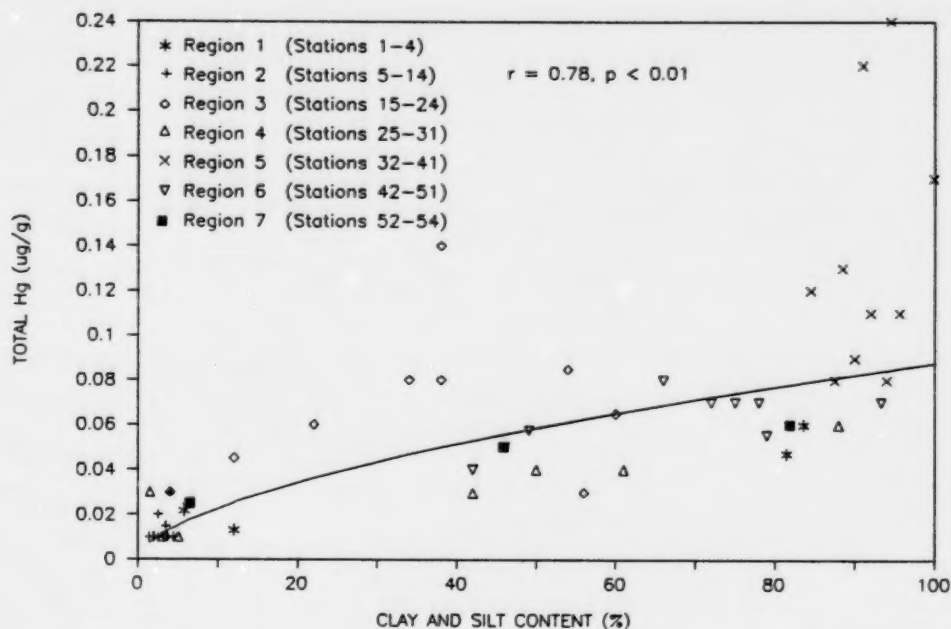
Region 7 (Stations 52 to 54) was located downstream of the City of Prince Albert sewage outfall, near the Weyerhaeuser pulp mill outfall. The total Hg concentration (0.06 ug/g) at Station 52, just upstream of the mill, is similar to the values of 0.03 and 0.05 ug/g downstream of the mill at Stations 53 and 54. These three values are similar to Hg levels found elsewhere in the river system. This mill, which began operation in 1968, was not likely a past contributor of Hg to the river since pulp mills stopped using mercurials around 1970 (Sherbin 1979).

The 1984 sediment results for the following parameters are presented in Appendix 2: iron, manganese, chloride, total carbon and total kjeldahl nitrogen. These parameters were analyzed because of their reported relationships with total Hg and CH_3Hg^+ (Jackson and Woychuk 1980; Rust and Waslenchuk 1976). No discernible relationships were found. Therefore, these nonmercury parameters were not analyzed in 1985. Sediment particle size and total Hg were, however, significantly correlated. Figure 5 shows increasing clay and silt content (decreasing particle size) versus increasing total Hg concentration. Increasing Hg levels versus decreasing particle sizes have also been reported for sediments from the South Saskatchewan River (Hwang 1978) and from other other aquatic systems (Creclius et al. 1975; Rust and Waslenchuk 1976).

7.1.2 Methylmercury

Methylmercury concentrations for the 54 stations are shown in Figure 6. Methylmercury percent fractions ($\text{CH}_3\text{Hg}^+/\text{total Hg} \times 100$) for 53 of the 54 stations are shown in Figure 7. Methylmercury percent fractions are shown as inequalities where total or methyl mercury values are less than detectable. The CH_3Hg^+ percent fraction for Station 11 was not determined since

FIGURE 5 TOTAL Hg VERSUS SEDIMENT CLAY AND SILT CONTENT



total Hg and CH_3Hg^+ values were both less than detectable.

Methylmercury levels in Region 1 (Stations 1 to 4) are higher at Lake Diefenbaker Stations 1 and 2 than at Stations 3 and 4 upstream of Saskatoon: 0.89 and 0.56 ng/g vs <0.10 and <0.10 ng/g. The CH_3Hg^+ percent fractions for Region 1 are less than 2%. As shown in Figure 7, the CH_3Hg^+ fractions for Region 1 are typical of the corresponding values for the other lakes sampled (Regions 4 to 6) with the exception of Stations 44 and 47. These two anomalies are discussed later in this section.

Methylmercury levels in the upper part of Region 2 show a pronounced increase over levels found at Stations 3 and 4, just upstream of Saskatoon. Despite similarities in sampling methods, sediment clay and silt content, and total Hg values for Region 2 (Stations 5 to 14), the relatively high CH_3Hg^+ values at Stations 5 to 9 diminish to less than detectable values (<0.10 ng/g) at Stations 10 to 14. This difference between these two groups of

FIGURE 6 CH_3Hg^+ (ng/g dry wt.) IN SASKATCHEWAN RIVER SYSTEM SEDIMENTS

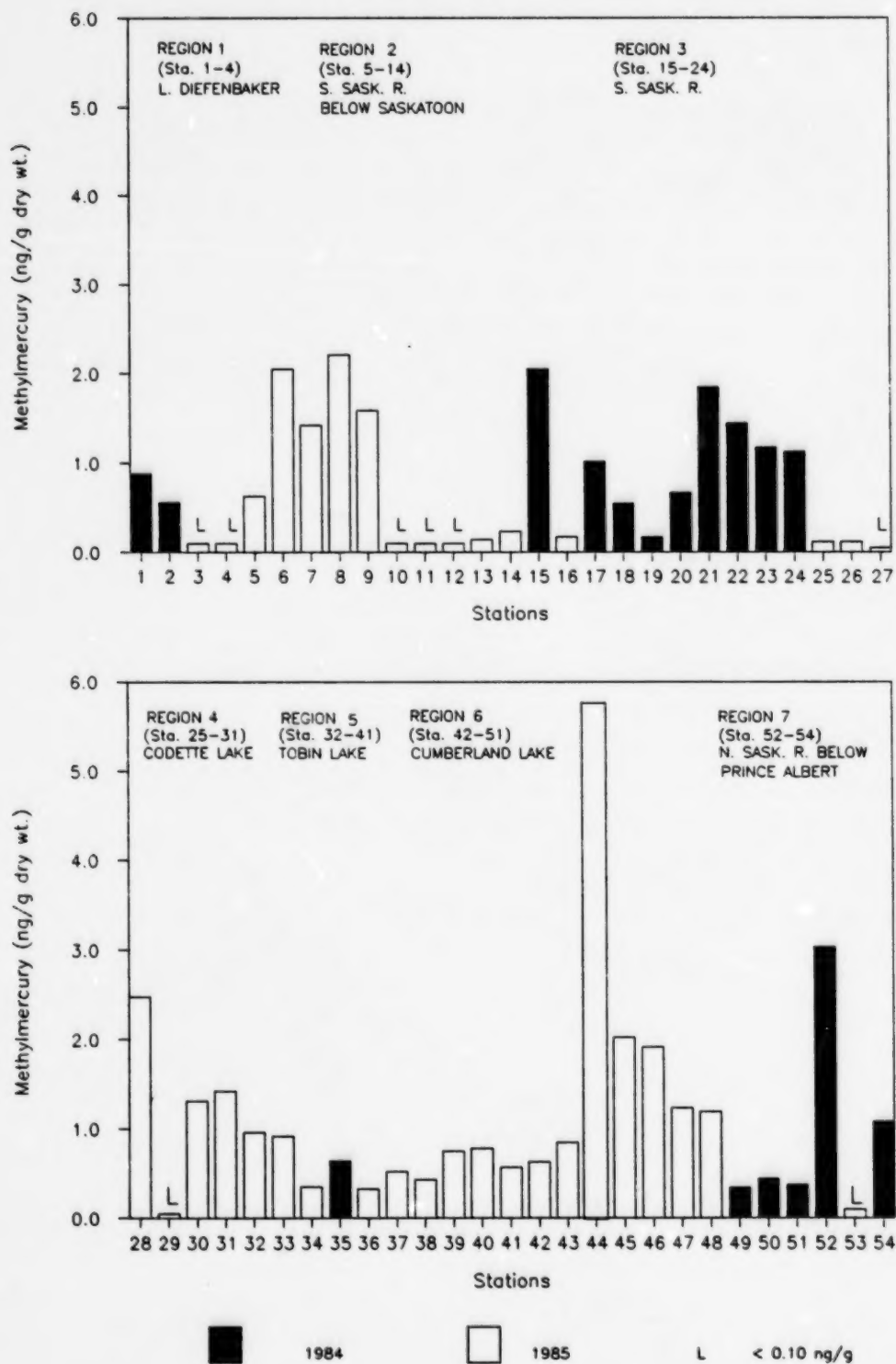
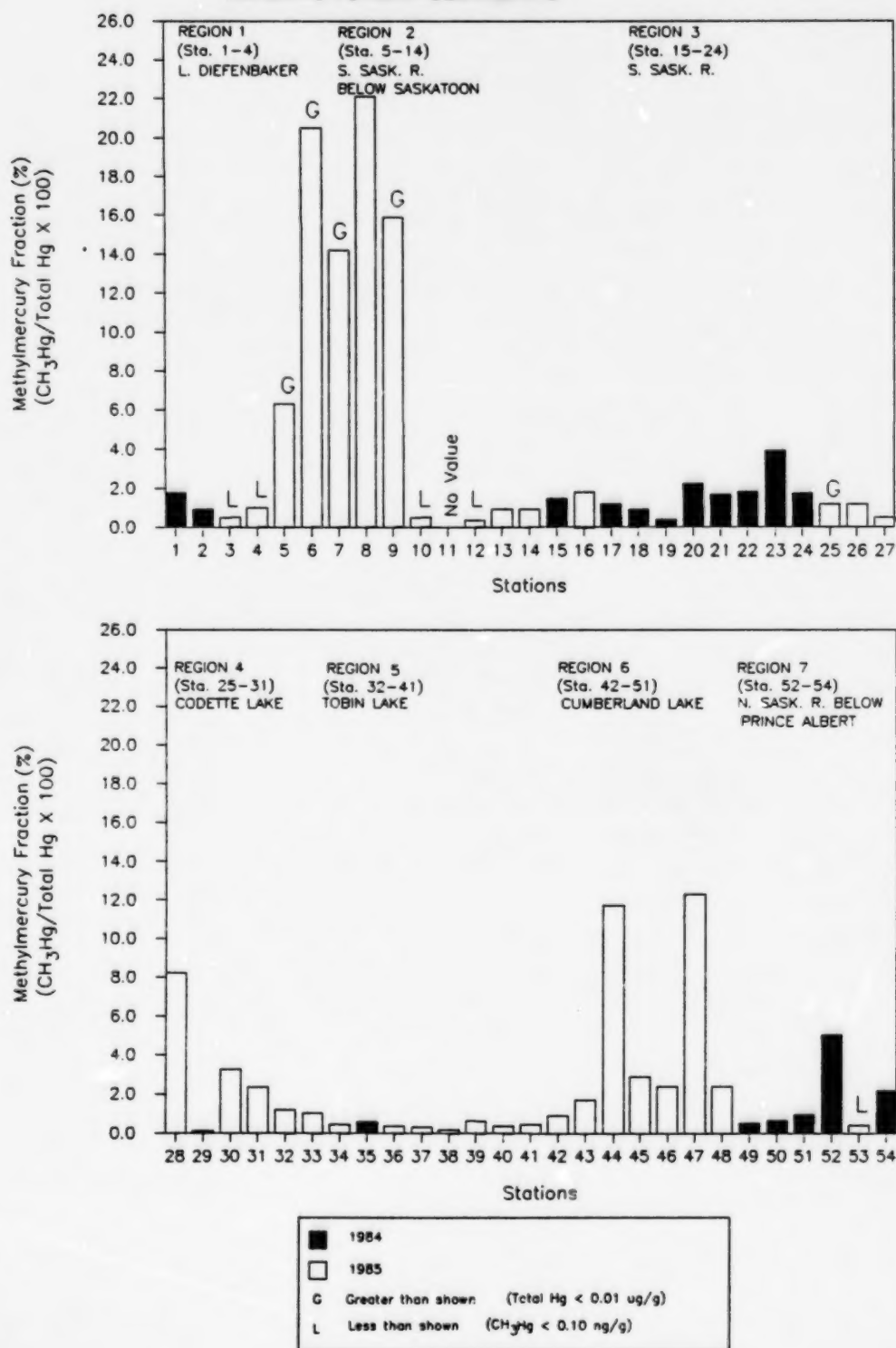


FIGURE 7 CH_3Hg^+ FRACTION OF TOTAL Hg IN SASKATCHEWAN
RIVER SYSTEM SEDIMENTS



stations is shown more distinctly by their corresponding CH_3Hg^+ fractions (Figure 7).

Methylmercury levels in Region 3 (Stations 15 to 24) range between 0.17 and 2.05 ng/g. Unlike other regions, CH_3Hg^+ values in Region 3 appear to be a function of the amount of total Hg present; higher total Hg values correspond to higher CH_3Hg^+ values. The CH_3Hg^+ fractions are approximately 2% throughout Region 3.

Methylmercury concentrations detected in Region 4 (Stations 25 to 31) range between <0.10 and 2.47 ng/g. No discernible pattern is evident between these values and corresponding levels of total Hg.

Region 5 (Stations 32 to 41) possesses the narrowest range of CH_3Hg^+ values of all the regions: 0.33 to 0.96 ng/g. The average CH_3Hg^+ fraction for this region is the lowest (1.2%) of all the regions. Region 5 sediments were analyzed at various depths for CH_3Hg^+ (Table 8). No perceptible trend is evident for CH_3Hg^+ with depth. There is also no trend between CH_3Hg^+ and corresponding levels of total Hg (Table 8).

Region 6 (Stations 42 to 51) possesses generally higher levels of CH_3Hg^+ than Region 5: 0.34 to 5.83 vs 0.33 to 0.96 ng/g. The highest CH_3Hg^+ value (5.83 ng/g) in the system is at Station 44. The CH_3Hg^+ fractions in Region 6 are generally less than 3% except at Stations 44 and 47, where the values are 11.6% and 12.3% respectively; these are the only two stations whose sediments were comprised of Sphagnum moss.

Methylmercury values for Region 7 (Stations 52 to 54) are 3.03, <0.10 and 1.08 ng/g respectively. The low value at Station 53, immediately downstream of the Weyerhaeuser mill effluent, may be due to methylation inhibition as a result of this effluent.

To account for variation in CH_3Hg^+ levels, CH_3Hg^+ was

correlated with corresponding concentrations of total Hg for all the stations. A low correlation ($r=0.33$, $p<0.05$) was found as shown in Figure 8. Lack of a good correlation between total Hg and CH_3Hg^+ has been observed in other lake-river systems (Jackson 1986; Jackson and Woychuk 1980).

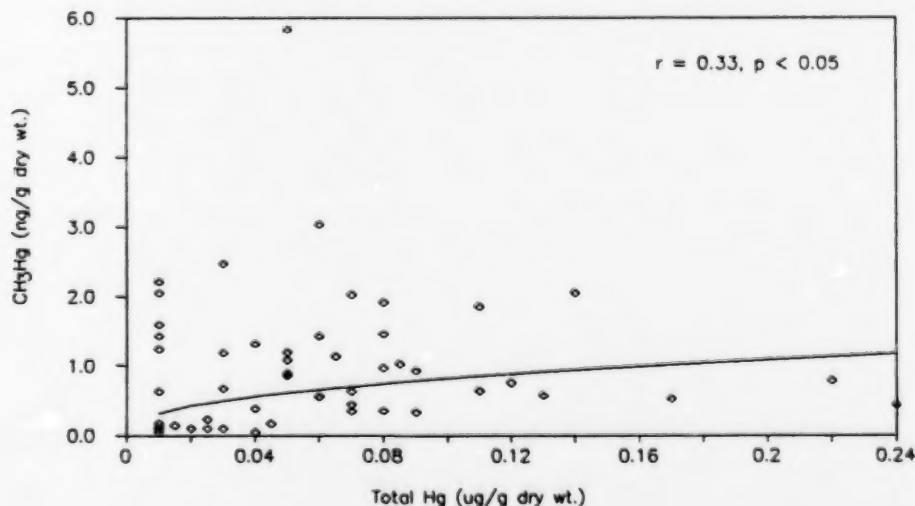
Data shown in Figures 4, 5 and 6 for total Hg, particle size and CH_3Hg^+ are presented in Appendix 3.

Total and methyl mercury concentrations in the sediments of the seven Regions are summarized in Table 9. Total Hg is generally higher in Region 5 (Tobin Lake) while total Hg is the lowest in Region 2, which previously possessed high Hg concentrations. The CH_3Hg^+ median values for the seven regions are typically <2 ng/g.

7.2 Water

The 1984 results of the nonmercury parameters are presented in Appendix 4. The 1984 results led to several changes in the 1985 water sampling program; the nonmercury parameters were dropped, the detection limit for total Hg was lowered from 0.2 to

FIGURE 8 TOTAL Hg VERSUS CH_3Hg^+ IN BOTTOM SEDIMENTS



0.02 ug/L, and unfiltered water samples were analyzed for CH_3Hg^+ .

7.2.1 Total and Methyl Mercury in Water

The 1984 total Hg values are below the detection limit of <0.2 ug/L. The 1985 samples, taken immediately above and below Saskatoon, are less than the total Hg detection limit of 0.02

TABLE 9
TOTAL AND METHYL MERCURY CONCENTRATIONS IN SURFICIAL
BOTTOM SEDIMENTS - SASKATCHEWAN RIVER SYSTEM (1984 & 1985)

Region (Station)	Total Hg (ug/g dry wt.)			CH_3Hg^+ (ng/g dry wt.)		
	Median	Range	N	Median	Range	N
1 (1-4)	0.04	0.01-0.06	4	0.31	<0.10-0.89	4
2 (5-14)	0.01	<0.01-0.03	10	0.43	<0.10-2.21	10
3 (15-24)	0.07	0.01-0.14	10	1.08	0.17-2.05	10
4 (25-31)	0.03	<0.01-0.06	10	0.12	<0.10-2.47	10
5 (32-41)	0.12	0.08-0.24	8	0.61	0.33-0.96	8
6 (42-51)	0.06	0.01-0.08	10	1.02	0.34-5.83	10
7 (52-54)	0.05	0.03-0.06	3	1.08	<0.10-3.03	3

Region:

- 1 S. Saskatchewan R. - upstream of Saskatoon
- 2 S. Saskatchewan R. - Saskatoon Chemicals to Clarkboro Ferry
- 3 S. Saskatchewan R. - Clarkboro Ferry to Confluence
- 4 Saskatchewan R. - confluence to Codette Lake
- 5 Tobin Lake
- 6 Codette Lake
- 7 N. Saskatchewan R. - downstream of Prince Albert

ug/L. Total Hg results for both years are presented in Table 10 along with CH_3Hg^+ data obtained in 1985. The CH_3Hg^+ level at Station 3, upstream of Saskatoon, is lower than the other values downstream of Saskatoon: 0.16 vs 0.25 to 0.58 ng/L. These few data, however, do not permit any definite conclusions to be made concerning the presence of higher CH_3Hg^+ concentrations in the river below Saskatoon.

7.3 Biota

Samples of macrophytes and crayfish were collected at most of the 1984 stations. Samples of crayfish were also collected in 1985 from some stations in Regions 3 and 6. Macrophyte and crayfish data are reported on a dry wt. and wet wt. basis respectively.

7.3.1 Crayfish

Concentrations of total Hg in crayfish samples ranged from 110 ng/g at Station 4 to 560 ng/g at Station 12. The range of CH_3Hg^+ was from 33.4 ng/g at Station 4 to 165.7 at Station 24. The lowest total and methyl mercury values were measured in crayfish taken immediately upstream of Saskatoon. The concentrations of total Hg and CH_3Hg^+ in crayfish were not significantly correlated ($p > 0.05$) with those in the sediments.

7.3.2 Macrophytes

Total Hg levels range between 0.016 and 0.072 ug/g, and CH_3Hg^+ levels range between <0.50 ng/g and 2.34 ng/g in the macrophytes (Table 11). Where CH_3Hg^+ was detected, CH_3Hg^+ comprised 3.5% of the total Hg, on average. Total Hg levels in the macrophytes are poorly correlated ($r = 0.06$, $p > 0.05$) with Hg in the sediments. This observation supports the finding of Eriksson and Mortimer (1975); Hg uptake in rooted plants occurs primarily from the surrounding water.

TABLE 10
MERCURY IN WATER SAMPLES (1984 & 1985)

Station	Total Hg (ug/L)	CH_3Hg^+ (ng/L)
1	<0.2	NS ^a
2	<0.2	NS
3 ^b	<0.02	0.16
5 ^b	<0.02	0.28
6 ^b	<0.02	0.35
7 ^b	<0.02	0.28
8 ^b	<0.02	0.48
9 ^b	<0.02	0.57
10 ^b	<0.02	0.25
14 ^b	<0.02	0.58
15	<0.2	NS
17	<0.2	NS
18	<0.2	NS
19	<0.2	NS
20	<0.2	NS
21	<0.2	NS
22	<0.2	NS
23	<0.2	NS
24	<0.2	NS
35	<0.2	NS
49	<0.2	NS
50	<0.2	NS
51	<0.2	NS
53	<0.2	NS
54	<0.2	NS

a Not Sampled
b 1985 Data

8.0 DISCUSSION

Total and methyl mercury levels in sediment, biota and water are discussed in relation to historical data for the Saskatchewan River System and other aquatic systems affected by Hg.

Mercury in a river-lake system is subject to environmental factors that affect its movement and concentration. These factors include the suspension, transport and deposition of sediment-bound Hg and its transfer from bed sediment to the water and atmosphere. Therefore, Hg concentrations will undoubtedly change with time.

APPENDIX 1 SAMPLE STATION DESCRIPTION

Station No.	Location and Description
1	- Lake Diefenbaker (108° 15' 30" 50° 40' 00") - 25 m from S. shore along 100 m transect parallel to shore - Composite of 6 cores ¹ (0-15 cm)
2	- Lake Diefenbaker (108° 05' 20" 50° 40' 30") - S. shore, near inlet along 200m transect - Composite of 6 cores ¹ (0-15 cm)
3	- S. Saskatchewan River, upstream of Saskatoon - 1 km (upstream of Queen Elizabeth Power Station (QEPS)) - Between W. shore and Yorath I. - Composite of 6 cores ² (0-15 cm)
4	- S. Saskatchewan River, 100 m downstream of QEPS outfall - Composite of: 1) 3-15 cm cores ² (60 yds from W. shore) and 2) 3-13 cm cores ² from middle of river
5	- S. Saskatchewan River, downstream of Saskatoon Chemical (SC) outfall - 3 transects; 0.3 km, 0.7 km and 1.4 km downstream of SC - 9 cores per transect - Composite of 27 cores ² (0-10 cm)
6	- S. Saskatchewan River - 3 transects; 2.0 km, 2.5 km and 3.5 km downstream of SC - 9 cores per transect - Composite of 27 cores ² (0-12 cm)
7	- S. Saskatchewan River - 1 transect (9 cores): 4 km downstream of SC - 3 cores near S. shore, 4.8 km downstream of SC - 3 cores near S. shore, 5.3 km downstream of SC - Composite of 15 cores ² (0-12 cm)
8	- S. Saskatchewan River - 3 transects: 5.8 km, 6.9 km and 7.3 km downstream of SC - 9 cores per transect - Composite of 27 cores ² (0-10 cm)

1 sampled with a KB corer
2 sampled with a Livingston piston corer

Station No.	Location and Description
9	- S. Saskatchewan River - 3 transects: 8.0 km, 8.6 km and 9.6 km downstream of SC - 9 cores per transect - Composite of 27 cores ² (0-10 cm)
10	- S. Saskatchewan River - 3 transects: 10.3 km, 10.8 km and 11.4 km downstream of SC - 9 cores per transect - Composite of 27 cores ² (0-12 cm)
11	- S. Saskatchewan River - 1 transect (9 cores): 12.7 km downstream of SC - 3 cores, 20 m from N. shore, 13.6 km downstream of SC - 3 cores, 20 m from N. shore, 18.8 km downstream of SC - Composite of 15 cores ² (0-12 cm)
12	- S. Saskatchewan River - 1 transect 14.7 km downstream of SC - Composite of 9 cores ² (0-10 cm)
13	- S. Saskatchewan River - 3 transects: 15.9 km, 16.9 km and 18.0 km downstream of SC - Composite of 27 cores ² (0-12 cm)
14	- S. Saskatchewan River, between train tressel and Clarkboro ferry - Composite of 9 cores, ² 20 m from E. shore, (0-10 cm)
15	- S. Saskatchewan River at Clarkboro ferry - 20 m downstream of berm, 40 m from W. shore - Composite of 6 cores ² (0-10 cm)
16	- S. Saskatchewan River (106° 20' 40" 52° 49' 10") - Cores taken from sandbar in middle of river across from Station 4 - 10 cores along W. side, 10 cores along E. side of sandbar - Composite of 20 cores (0-60 cm), sampled by an Oakfield sampler

1 sampled with a KB corer
2 sampled with a Livingston piston corer

TABLE 11
MERCURY IN MACROPHYTES AND CRAYFISH (1984 & 1985)

Station (ng/g)	Macrophyte ^a (dry wt.)		Crayfish ^b (wet wt.)	
	Total Hg (ug/g)	CH ₃ Hg ⁺ (ng/g)	Total Hg (ng/g)	CH ₃ Hg ⁺
1	0.027 ^g	<0.50 ^g	NS ^d	NS
4 ^c	NS	NS	110	33.4
5 ^c	NS	NS	240	102.6
6 ^c	NS	NS	240	110.0
8 ^c	NS	NS	270	125.2
9 ^c	NS	NS	200	91.0
10 ^c	NS	NS	230	53.5
11 ^c	NS	NS	390	164.9
12 ^c	NS	NS	560	88.2
13 ^c	NS	NS	410	144.5
14 ^c	NS	NS	120	54.8
25 ^c	NS	NS	140	49.6
15	0.036 ^h	1.04 ^h	143	74.0
17	0.026 ^h	<0.50 ^h	151	63.4
18	0.032 ^h	1.79 ^h	153	72.0
19	0.052 ^h	<0.50 ^h	133	72.9
20	0.037 ^h	<0.50 ^h	413	150.9
21 ^e	0.016 ^h	<0.50 ^h	181	101.1
21 ^f	0.035 ^h	<0.50 ^h	234	120.7
22	0.072 ^h	1.16 ^h	145	86.2
23	0.016 ^h	<0.50 ^h	162	88.4
24	0.051 ^h	2.34 ^h	428	165.7
49	0.047 ⁱ	1.38 ⁱ	NS	NS
50	0.016 ^j	<0.50 ^j	NS	NS
51	0.016 ^g	<0.50 ^g	NS	NS

a Composite of leaves

b Composite of abdominal muscles

c 1985 Data

d Not sampled

e South shore

f North shore

g Polygonum coquimbense

h Scirpus sp.

i Potamogeton Richardsonii

j Potamogeton pectinatus

Total Hg levels in sediments along an 8.8 km reach (Stations 5 to 9) downstream of Saskatoon Chemicals have significantly decreased from 1971 levels, between 0.95 and 2.45 ug/g, to 1985 levels of ≤ 0.03 ug/g. These 1985 values are similar to historical total Hg values reported for sediments upstream of Saskatoon Chemicals: 0.033 ug/g (Bailey *et al.* 1971) and 0.0228 ug/g (Hwang 1978). As well, current total Hg sediment data for the entire South Saskatchewan River are similar to total Hg data reported

for the Alberta portion of the North Saskatchewan River (Munson and Daniel 1973; Ramamoorthy et al. 1985). Unlike the South Saskatchewan River, the North Saskatchewan River has not received a large input of Hg from a single point source but has received low amounts of Hg which, Ramamoorthy et al. (1985) suggest, originates from sources that include industrial and municipal discharges in Alberta. The South Saskatchewan River below Saskatoon can no longer be considered contaminated by high levels of Hg. In fact, the opposite condition now exists; Hg in this reach is similar to or below levels reported elsewhere in the Saskatchewan River System.

Total Hg concentrations in South Saskatchewan River sediments are likely best represented by Region 2 values since sampling for Region 3 was biased. Unlike Region 2, which was sampled at regular intervals regardless of substrate, sediments from Region 3 were taken from sites believed to be sediment deposition areas. This was shown by their higher clay and silt content; the average clay and silt content of Region 3 and 2 sediments are 37.5% and 4.2% respectively. The deposition sites in Region 3 constitute only a small area. Therefore, if Region 3 had been sampled like Region 2, lower total Hg levels would have been detected in Region 3 as well.

As shown in Table 9, total Hg values for Region 5 (Tobin Lake) sediments are noticeably higher than those for Region 2 which, as previously discussed, is considered to represent typical levels in the South Saskatchewan River below Saskatoon. The difference in total Hg between these two regions is more evident if the estimated amount of Hg, by weight, is considered. The amounts of total Hg in the South Saskatchewan River, below Saskatoon, and Tobin Lake are roughly estimated to be 0.1 and 22.6 tonnes respectively. These calculations are based on: 1) a median Hg value of 0.01 and 0.12 ug/g for the river and lake sediments respectively (Table 9); 2) an average river sediment depth of 11 cm and an average lake sediment depth of 30 cm; 3) a river and lake surface area of 67 and 313 km² respectively; and

4) a dry wt. sediment density of 2.0 g/cm^3 (Bailey et al. 1971). The average sediment depths assumed for the South Saskatchewan River and Tobin Lake are typical of those sampled in this survey. If the median Hg value of 0.06 ug/g is representative for Lake Diefenbaker, a major sink above the chlor-alkali plant, then the higher median concentration (0.12 ug/g) observed for Tobin Lake is, presumably, a result of other sources. This increase of 0.06 ug/g corresponds to one-half of the estimated 22.6 tonnes, or 11.3 tonnes, of Hg in Tobin Lake. It is interesting to note that the 11.3 tonnes is between 34% and 51% of the estimated Hg discharged from the chlor-alkali plant.

The range of total Hg values in sediments for Region 6 (Stations 42 to 51) are lower than for Region 5: 0.01 to 0.08 ug/g vs 0.08 to 0.24 ug/g . These ranges are within the range of 0.001 to 0.345 ug/g of total Hg ($N^a=1076$) observed in lakes and streams for two areas of northern Saskatchewan (Arnold and Smith 1977). Since Region 5 (Tobin Lake) is the major sink for sediments transported down the Saskatchewan River System, most of the sediment-bound Hg is retained in Tobin Lake.

Methylmercury levels in bottom sediments are influenced by variables which include methylation and demethylation rates and sorption and desorption capacities of the sediments. Like total Hg levels in sediments, the CH_3Hg^+ levels in sediment will also change with time.

Methylmercury values throughout the study area are typically less than 2 ng/g and correspond to less than three percent of total mercury. The CH_3Hg^+ values are similar to or below CH_3Hg^+ levels reported for river-lake systems affected by anthropogenic sources of Hg (Jackson 1986; Jackson and Woychuk 1980; Batti et al. 1975; Longbottom et al. 1973). Although the CH_3Hg^+ values are low, CH_3Hg^+ percent fractions at some stations are higher than three percent. This may be attributed to high methylation rates. Furtuani and Rudd (1980) showed that microbial substrate utilization increased with increased methylation rates.

Similarly, Jackson and Woychuk (1980) attributed higher rates of methylation in bottom sediments to the amount of total nitrogen present. Municipal sewage in rivers may also influence methylation rates in sediments. Langley (1973) observed the highest methylation rates in contaminated river sediments, from a chlor-alkali plant, below a city with no municipal waste treatment.

The highest CH_3Hg^+ fractions, observed at Stations 5 to 9 and Stations 44 and 47, may be due to the higher availability of nutrients and higher microbial activity at these sites. Stations 5 to 9 are located within 10 km downstream from the Saskatoon sewage plant. This plant is known to have a significant nutrient impact on the river, extending 28 km downstream (Tones *et al.* 1980). The higher CH_3Hg^+ percent fractions for Stations 44 and 47 may be due to the higher microbial activity and nutrients associated with the Sphagnum moss which was found only at these two stations. Sphagnum moss has been shown to increase the methylation activity in the water column and surface sediments under enclosure experiment conditions (Rudd *et al.* 1983).

Although data for crayfish are limited, a comparison with crayfish data from other river systems is possible. The average total Hg (wet wt.) concentration in crayfish is similar to that reported by Munro and Gummer (1980) for a contaminated Saskatchewan creek: 0.24 ± 0.13 ug/g, $N^a=10$ (Table 11) vs 0.22 ± 0.06 ug/g ($N^b=10$). Both results are, however, considerably less than Hg levels detected in crayfish from the contaminated English-Wabigoon River System in the vicinity of Clay Lake. There, 13 composite (abdominal muscle) samples, comprised of four subsamples, yielded between 1.43 and 7.36 ug/g (wet wt.) of total Hg. Background total Hg (wet wt.) levels in 9 composite samples, comprised of four subsamples taken from the Wabigoon River above Dryden and from a tributary river, were between 0.09 and 0.27 ug/g (Hamilton 1972).

Total Hg levels in South Saskatchewan River water samples taken in 1985 were similar to historical data for the river; all results were less than 0.02 ng/L. A good indication of total Hg concentrations in the North Saskatchewan River was not attained due to the few water samples taken and the high detection limit (≤ 0.2 ug/L) used in 1984. Ramamoorthy *et al.* (1985) reported higher total Hg levels in water from the North Saskatchewan River than previously reported anywhere in the Saskatchewan River System. This finding is important since fish bioaccumulate Hg from the water column. If Ramamoorthy's data are valid, Hg in North Saskatchewan River fish would be expected to contain higher Hg concentrations than fish of the same species in the South Saskatchewan River. A review of the fish data shows, however, that fish in the South Saskatchewan River generally possess the highest Hg levels in the entire river system despite low Hg levels in the water. Mercury concentrations in fish can exceed 0.5 ug/g (wet wt.) in waters that have low Hg levels. For instance, increased Hg levels were observed in fish in the lakes flooded by the Churchill River diversion in Northern Manitoba despite low Hg levels in these waters. Seventeen sites sampled throughout the diversion, between 1978 and 1981, contained less than 0.005 ug/L of total Hg, and 13 of 14 water samples contained less than 0.2 ng/L of CH_3Hg^+ (Bodaly *et al.* 1984). These CH_3Hg^+ values are lower than those reported in this study; eight water samples collected from the South Saskatchewan River below Saskatoon averaged 0.36 ng/L and ranged between 0.16 and 0.58 ng/L.

In summary, from 1971 to 1985, Hg levels in South Saskatchewan River sediments previously contaminated by Hg from a Saskatoon chlor-alkali plant have decreased by approximately two orders of magnitude. Current concentrations of total Hg are similar to historical background levels upstream of Saskatoon and for the North Saskatchewan River. The roughly estimated 0.1 tonnes of Hg in the South Saskatchewan River below Saskatoon is small in relation to the estimated 22 to 33 tonnes of Hg

discharged from the Saskatoon chlor-alkali plant. Most of the chlor-alkali Hg still in the Saskatchewan River System appears to be contained in Tobin Lake sediments. Despite the Hg decline in South Saskatchewan River sediments and the absence of a significant Hg source to this river, Hg levels in South Saskatchewan River fish have not substantially declined.

9.0 CONCLUSIONS

The most significant source of Hg to the South Saskatchewan River in the past was from Saskatoon Chemicals, which operated between 1962 and 1978 as a chlor-alkali plant. Currently, Saskatoon Chemicals, the City of Saskatoon and nonpoint Saskatchewan sources are not considered significant Hg contributors to the South Saskatchewan River.

Current Hg concentrations in South Saskatchewan River sediments are typical of historical concentrations found upstream of Saskatoon Chemicals and similar to 1981 levels reported for the North Saskatchewan River in Alberta. Total Hg concentrations have decreased along a 8.8 km reach of the South Saskatchewan River below Saskatoon Chemicals: from 0.95 to 2.45 ug/g (dry wt.), in 1971, to current levels less than 0.03 ug/g (dry wt.). The highest Hg concentrations in sediments for the Saskatchewan River System (0.08 to 0.24 ug/g dry wt.) were detected in Tobin Lake. The lower total Hg concentrations downstream in Cumberland Lake (0.01 to 0.08 ug/g dry wt.) and the Hg decrease in South Saskatchewan River sediments indicate the majority of Hg transported down the Saskatchewan River System has been retained in Tobin Lake sediments.

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Station No.	Location and Description
17	- S. Saskatchewan River (106° 20' 40" 52° 26' 10") - 15 m downstream of irrigation berm, 15 m from W. shore - Composite of 10 cores² (0-10 cm)
18	- S. Saskatchewan River at Hague ferry - 50 m downstream of berm, 7 m from S. shore - Composite of 6 cores² (0-10 cm)
19	- S. Saskatchewan River (106° 05' 10" 52° 49' 10") - E. side of island, 20 m into inlet - Composite of 6 cores² (0-15cm)
20	- S. Saskatchewan River at St. Laurent ferry - 18 m downstream of berm, 18 m from W. shore - Composite of 6 cores² (0-20 cm)
21	- S. Saskatchewan River at Fenton ferry - 18 m downstream of berm, 5 m from S. shore - Composite of 6 cores² (0-3 cm) - 60 m downstream of berm, 3 m from N. shore - Composite of 6 cores² (0-8 cm)
22	- S. Saskatchewan River at Muskoday Bridge - Approx. 300 m upstream, in inlet along W. shore - Composite of 6 cores² (0-13 cm)
23	- S. Saskatchewan River at Birch Hills ferry - 500 m downstream of berm at entrance of inlet on S. shore at river bend - Composite of 6 cores² (0-20 cm)
24	- S. Saskatchewan River at Weldon ferry - 6 m downstream of berm, 3 m off W. shore - Composite of 6 cores² (0-15 cm) - 40 m downstream of berm, 3 m off N. shore - Composite of 6 cores² (0-13 cm)
25	- Saskatchewan River at Gronlid Ferry, S. shore - Downstream side of berm - Composite of 9 cores² (0-12 cm)
26	- Saskatchewan River at Gronlid ferry, S. shore - W. side of sandbar across from station 32 - Composite of 8 cores² (0-10 cm)
27	- Codette Reservoir (104° 18' 30") - One Ponar sample

1 sampled with a KB corer

2 sampled with a Livingston piston corer

Station No.	Location and Description
28	- Codette Reservoir (104° 14' 20") - Composite of 2 Ponar samples
29	- Codette Reservoir (104° 10' 05") - Composite of 2 Ponar samples
30	- Codette Reservoir (104° 05' 50") - Composite of 3 Ponar samples
31	- Codette Reservoir (104° 04' 40") - Approximately 500 m upstream of dam - Composite of 2 Ponar samples
32	- Tobin Lake, (N.W transect bearing from 103° 56' 15" 53° 28' 05" - Composite of 2 equidistant cores ¹ (0-13 cm) - Water depth; 2 m & 9 m
33	- Tobin Lake N.W.N. transect bearing from 103° 52' 30" 53° 28' 05" - Composite of 3 equidistant Ekman samples - Water depth; 12 m, 12 m, & 7 m
34	- Tobin Lake N.W. transect from point at 103° 49' 30" 53° 29' 23" - 4 equidistant cores ¹ : (a) top fraction (0-13 cm) bottom fraction (13-28 cm) water depth; 3 m (b) top fraction (0-13 cm) middle fraction (13-23 cm) bottom fraction (23-35 cm) water depth; 4 m (c) top fraction (0-13 cm) bottom fraction (13-25 cm) water depth; 7 m (d) top fraction (0-13 cm) bottom fraction (13-23 cm) water depth; 12 m
35	- Tobin Lake (103° 46' 53" 31) - Transect along N.W. bearing - Composite of 6 cores ¹ (0-15 cm) - Composite of 6 cores ¹ (15-40 cm) - Water depth: 7 m

¹ sampled with a KB corer

² sampled with a Livingston piston corer

Station No.	Location and Description
36	- Tobin Lake, transect on N.W. bearing from Tobin Lake Resort - 5 cores¹: (a) top fraction (0-13 cm) bottom fraction (13-23 cm) (b) top fraction (0-13 cm) middle fraction (13-23 cm) bottom fraction (23-33 cm) water depth; 14 m (c) top fraction (0-13 cm) middle fraction (13-25 cm) bottom fraction (25-32 cm) water depth; 8 m (d) top fraction (0-13 cm) middle fraction (13-23 cm) bottom fraction (23-36 cm) water depth; 7m (e) top fraction (0-13 cm) bottom fraction (13-20 cm) water depth; 15 m
37	- Tobin Lake (330° transect bearing from S. shore at Pas Trail) - Composite of 5 cores¹ (top fraction: 0-13 cm bottom fraction: 13-20 cm) - Water depth: 13 m, 12 m, 11 m, 16m, & 11 m
38	- Tobin Lake (330° transect bearing from S. shore at 103° 7' 10" 53° 36' 57") - Composite of 5 cores¹ (0-8 cm) - Water depth: 11 m, 11 m, 19 m, 16 m, & 6 m
39	- Tobin Lake (transect bearing 20°E. of N. from S. shore at 103° 32' 40" 53° 36' 32") - 5 Composite cores¹ (0-12 cm), 1 core¹ (13-18 cm) - Water depth; 11 m, 10 m, 17 m, 19 m, & 5 m
40	- Tobin Lake (transect bearing 250° from N. shore peninsula at 103° 24' 30" 53° 37' 55") - Composite of 3 Ekman grabs, equidistant to midway into lake - Water depth: 22 m, 12 m, 10 m

1 sampled with a KB corer

2 sampled with a Livingston piston corer

Station No.	Location and Description
41	- Tobin Lake (transect bearing due E. 1.75 km upstream of Nipawin dam) - Composite of 3 equidistant composite cores¹: 2 Composite core top fractions (0-13 cm) - water depth: 13 m 2 Composite core middle fractions (13-25 cm) - water depth: 21 m 2 Composite core bottom fractions (25-33 cm) - water depth: 22 m
42	- Cumberland Lake 102° 19' 20" 54° 04' 45" - 2 composite cores² (0-13 cm) - Water depth: 1 m
43	- Cumberland Lake 102° 18' 55" 54° 04' 50" - 2 composite cores² (0-13 cm) - 3 composite cores (13-30 cm) - Water depth: 3.3 m
44	- Cumberland Lake 102° 17' 50" 54° 04' 50" - 3 composite cores² (0-13 cm) - Water depth: 3.3 m
45	- Cumberland Lake 102° 16' 40" 54° 04' 50" - 2 composite cores² (0-13 cm) - Water depth: 1.3 m
46	- Cumberland Lake 102° 17' 15" 54° 04' 50" - 1 core² (0-13 cm) - Water depth: 1.4 m
47	- Cumberland Lake 102° 17' 50" 54° 03' 05" - 3 composite cores² (0-13 cm) - Water depth: 1 m
48	- Cumberland Lake 102° 18' 30" 54° 02' 15" - 3 composite cores² (0-13 cm) - Water depth: 1.4 m
49	- Cumberland Lake at mouth of Bigstone River - Composite of 6 cores² (0-15 cm)
50	- Bell Island on Old Channel of Saskatchewan River - 30 m from downstream tip of island, middle of channel - Composite of 6 cores² (0-15 cm)

1 sampled with a KB corer

2 sampled with a Livingston piston corer

Station No.	Location and Description
51	- Entrance of Old Channel (on N. side of Bell Island) to Saskatchewan River - Composite of 3 cores² (0-25 cm)
52	- Willow Island on N Saskatchewan River - N. side of island, 300 m from upstream end, approx 500 m upstream of PAPCO effluent - Composite of 6 cores² (0-5 cm)
53	- N. Saskatchewan River - 150 m downstream of Prince Albert Pulp Co. Ltd. effluent discharge - 12 grabs taken along mudflat on N. shore - Composite of 12 grabs taken at surface with trowel (0-13 cm)
54	- Island on N Saskatchewan River, 1.5 km downstream of PAPCO effluent - N. inlet to island - Composite of 6 cores² (0-60 cm)

1 sampled with a KB corer

2 sampled with a Livingston piston corer

APPENDIX 2
CHEMICAL ANALYSES OF BOTTOM SEDIMENTS (1984)
 (Percent by Weight)

Station	Fe	Mn	TC	TKN	CI
1	2.6	0.046	8.1	0.18	0.001
2	3.3	0.052	7.9	0.12	0.006
15	1.7	0.031	4.0	0.14	0.029
17	1.8	0.036	4.7	0.098	0.070
18	1.4	0.030	2.9	0.068	0.011
19	1.1	0.022	1.6	0.030	0.007
20	0.8	0.021	1.1	0.027	0.008
21	1.5	0.040	5.1	0.23	0.050
22	1.7	0.044	4.9	0.13	0.031
23	1.9	0.045	4.7	0.15	0.013
24	2.2	0.046	6.5	0.16	0.017
35	3.5	0.065	11.0	0.23	0.027
49	2.3	0.052	6.0	0.12	0.002
50	2.9	0.070	6.4	0.10	0.003
51	1.7	0.037	4.2	0.088	0.009
52	2.5	0.050	8.1	0.18	0.005
54	1.9	0.038	4.4	0.085	0.009

**APPENDIX 3
SEDIMENT DATA**

Station No.	Total Hg (ug/g dry wt.)	CH ₃ Hg (ng/g dry wt.)	clay and silt content (%)
1	0.05	0.89	82.0
2	0.06	0.56	84.0
3	0.02	<0.10	6.4
4	0.01	<0.10	12.4
5	<0.01	0.63	1.4
6	<0.01	2.05	4.4
7	<0.01	1.42	1.9
8	0.01	2.21	3.7
9	<0.01	1.59	2.5
10	0.02	<0.10	2.5
11	<0.01	<0.10	2.0
12	0.03	<0.10	4.0
13	0.02	0.14	3.5
14	0.03	0.23	6.0
15	0.14	2.05	38.0
16	0.01	0.17	3.5
17	0.09	1.02	54.0
18	0.06	0.55	22.0
19	0.05	0.17	12.0
20	0.03	0.67	4.0
21	0.11	1.85	34.0
22	0.08	1.45	38.0
23	0.03	1.18	56.0
24	0.07	1.13	60.0
25	<0.01	0.12	5.0
26	0.01	0.12	3.0
27	0.01	<0.10	2.0
28	0.03	2.47	42.0
29	0.04	<0.10	61.0
30	0.04	1.31	50.0
31	0.06	1.42	88.0
32	0.08	0.96	87.5
33	0.09	0.92	90.0
34	0.08	0.35	94.0
35	0.11	0.64	92.0
36	0.09	0.33	95.6
37	0.17	0.52	99.9
38	0.24	0.43	94.5
39	0.12	0.75	84.5
40	0.22	0.78	91.0
41	0.13	0.57	88.5
42	0.07	0.63	75.0
43	0.05	0.85	79.0
44	0.05	5.83	ND ^a
45	0.07	2.02	93.3
46	0.08	1.91	66.0
47	0.01	1.23	ND
48	0.05	1.19	46.0
49	0.07	0.34	72.0
50	0.07	0.44	78.0
51	0.04	0.38	42.0
52	0.06	3.03	82.0
53	0.03	<0.10	6.6
54	0.05	1.08	82.0

ND Not Determined

APPENDIX 4
WATER QUALITY RESULTS^a (1984)

Station	Fe	Mn	C	TKN	NO ₂ -N	NO ₃ -N	Cl	TNR ^b	VNR ^c
1	0.68	0.065	5	0.37	<0.01	<0.01	7.0	17	14
2	0.30	0.075	1	0.42	<0.01	<0.01	3.5	5	5
15	0.24	0.009	9	0.38	0.05	0.05	8.5	<1	<1
17	0.17	0.012	9	0.41	0.01	<0.01	9.3	5	1
18	0.08	0.010	7	0.36	<0.01	<0.01	8.2	1	<1
19	0.11	0.008	12	0.57	<0.01	<0.01	9.0	<1	<1
20	0.32	0.035	8	0.52	<0.01	<0.01	8.3	6	2
21	0.38	0.022	9	0.46	<0.01	<0.01	8.3	20	6
22	1.30	0.092	25	2.70	<0.01	<0.01	9.8	41	27
23	0.22	0.025	9	0.50	<0.01	<0.01	8.5	4	3
24	0.86	0.032	8	0.65	<0.01	<0.01	8.5	4	2
35	0.21	0.075	<1	0.80	<0.01	<0.01	6.3	8	7
49	5.00	0.100	8	0.75	<0.01	<0.01	4.6	120	33
50	0.28	0.040	5	0.61	<0.01	<0.01	8.9	8	6
51	3.00	0.095	6	0.92	<0.01	<0.01	7.7	116	23
53	0.76	0.098	2	0.73	<0.01	<0.01	4.4	16	7
54	1.00	0.060	1	0.60	<0.01	<0.01	4.1	39	12

a mg/l

b Total Nonfilterble Residue

c Volatile Nonfilterable Reside